

*Office of Technical Assistance Research Proposal*  
***Green Chemistry Alternatives to the Sulfate and Chloride Processes for  
Titanium Pigment Production***

## **Background**

Titanium dioxide is a white pigment that is widely used in many industry sectors, including coatings, cosmetics, plastics, and paper. Titanium dioxide's hallmark is its function as a hiding agent; it is considered to have the greatest hiding power (coverage) of all white pigments. More hiding power can mean lower film building requirements and consequently, reduced coating use. Titanium dioxide is itself noncombustible and nontoxic; for these reasons, it has replaced lead in many coating formulations. Nonetheless, titanium production is an expensive process, both in terms of environmental, health, and safety considerations and end-product economics. Formulation of a cleaner, more efficient synthesis pathway may reduce: a) risks to workers in the manufacturing plant; b) risk to the surrounding community; and c) vulnerability of American manufacturers in a global market.

### Titanium Dioxide Synthesis

Synthesis of titanium dioxide pigment occurs by one of the two following reactions; each takes place in two stages.

***Sulphate process:***  $\text{TiO}_2 \bullet \text{FeO} + 2 \text{H}_2\text{SO}_4 \rightarrow \text{TiOSO}_4 + \text{FeSO}_4 + 2 \text{H}_2\text{O}$  (ferrous sulphate is separated and  
(ilmenite ore) (titanyl sulphate) collected for sale as a raw material)

$\text{TiOSO}_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 \bullet \text{H}_2\text{O} + \text{H}_2\text{SO}_4$  (hydrate product is calcined at 800° C - 1000° C)

***Chloride process:***  $\text{TiO}_2 + \text{C} + 2 \text{Cl}_2 \rightarrow \text{TiCl}_4 + \text{CO}_2$  (reaction carried out under temperatures of 900° C)

$\text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2 + 2 \text{Cl}_2$  (chlorine gas is collected and recycled for a new batch)

The sulphate process can produce either the rutile or anatase form of titanium dioxide; the chloride process produces the rutile form only. The forms are distinguished from one another by their atomic packing --- rutile is more densely packed, and therefore tends to be more stable and has a higher refractive index. The higher refractive index of rutile and its higher resistance to degradation make it more suitable for paint formulation, whereas the anatase form is more widely used for paper coatings. The chloride process tends to predominate.

## **Scope of Problem**

### Environmental, Health, and Safety Impacts

Both the sulphate and chloride processes entail a host of environmental, health, and safety concerns in the plants where the titanium dioxide will be produced. In addition, these processes are energy --- and in the case of the sulphate process --- water intensive. A summary of environmental, health and safety concerns is as follows:

	Sulfate process	Chloride process
Toxic Release Inventory chemicals Toxics Use Reduction Act chemicals Clean Air Act --- Risk Management Program (RMP) Hazardous Air Pollutant (HAP)	<ul style="list-style-type: none"> <li>Sulfuric acid (<math>\text{H}_2\text{SO}_4</math>) in:               <ul style="list-style-type: none"> <li>Fuming form, aerosol form, and mixed w/ sulfur trioxide</li> </ul> </li> </ul>	<ul style="list-style-type: none"> <li>Titanium tetrachloride (<math>\text{TiCl}_4</math>)</li> <li>Chlorine gas (<math>\text{Cl}_2</math>)</li> </ul>
OSHA Permissible Exposure Limits (PELs)	<ul style="list-style-type: none"> <li>1 mg/ m<sup>3</sup> over an 8-hour period</li> </ul>	<ul style="list-style-type: none"> <li>Chlorine --- 3 mg/m<sup>3</sup> over any 15-min interval (ceiling limit)</li> </ul>
Energy use	<ul style="list-style-type: none"> <li>Titanyl sulfate reaction calls for removal of 1 mole of water per mole titanium dioxide generated; removal occurs at high temperatures, requiring high heat input.</li> </ul>	<ul style="list-style-type: none"> <li>Process occurs at high temperatures, requiring high heat input.</li> </ul>
Water use	<ul style="list-style-type: none"> <li>Step 2 requires 2 moles of water per mole of titanyl sulfate reacted.</li> </ul>	

U.S. titanium dioxide manufacturers must all submit plans under the Clean Air Act Risk Management Program. All facilities are subject to the most stringent tier of planning (Group 3). All plants that submitted an RMP reported at least one incident of worker injury due to chlorine gas release within the last 5 years. Thus, worker and community health and safety are a concern with current methods of titanium dioxide pigment production.

### Economics

Worldwide consumption of titanium dioxide pigment is expected to total 4.062 million metric tons in 2001; North America is expected to account for 34% of this consumption, and Western Europe at 31%. The United States alone is home to two of the top five producers --- DuPont and Kerr-McGee. Pressures on the titanium dioxide producers have included the stability of foreign currencies (specifically the euro), and supply chain issues. A weak euro has made it difficult for American pigment producers to export titanium dioxide pigments. In a recent article, a DuPont White Pigments and Mineral Products representative was quoted as saying: "Ten years ago, the difference between U.S. and European prices could literally be 25% or more than prices in the U.S. Now, U.S. prices are about 15% more than in Europe." (Chemical & Engineering News, October 9, 2000, p. 31). It was also stated that U.S. manufacturers are attempting to raise prices but are also looking for debottlenecking projects that can expand production at low cost. Given that the chloride and sulfate processes are both mature are carried out similarly on a global scale, the amount of debottlenecking that can occur along with the expected benefits is likely to be limited.

Coatings manufacturers have a difficult time passing on price increases to their customers, which increases their sensitivity to increases in pigment costs. Although Massachusetts does not have a strong

presence in titanium production, the end user market is substantial. A review of the Harris Massachusetts Manufacturers Directory for 1998 revealed an estimated 1,900 end users for coatings pigmented with titanium dioxide. The figure excluded the paper, wood, and textile industry sectors; of these sectors, wood furniture and fixtures may potentially add another 200 end users. Thus, supply chain economics suggests an incentive for cleaner synthesis of titanium dioxide.

## Objectives

The research may be framed around one of the following two objectives:

- 1) Develop a “green chemistry” technique for extraction of titanium dioxide from ilmenite and/or crystalline forms. The United States Environmental Protection Agency defines ‘green chemistry’ as “the design of chemical products and processes that are more environmentally benign”. In this instance, a green chemistry approach would be the replacement of the chloride process with a safer pathway.
- 2) Develop an alternative pigmenting process entirely --- casein (milk-protein based) pigments have been available for decades. Though it is based from sustainable material --- milk protein --- casein pigments often contain formalin (formaldehyde-based) additives, which lend durability to the pigment. The challenge in this case is to modify the casein base with more environmentally benign substitutes.

OTA can assist in the identification of an industry partner.

## Scope of Work

Alternative formulations would require testing in order to compare pigment performance against traditionally synthesized titanium dioxide.

- 1) Develop alternative pigment formulation
- 2) Screen reactants and products for regulated status and existing data on environmental and health effects
- 3) Assess yield as compared to the chloride process
- 4) Test pigment characteristics and compare to titanium dioxide synthesized by the chloride process
  - Density
  - Refractive index (as an indicator of opacity)
  - Specific surface area ( $\text{m}^2/\text{g}$  pigment)
  - Particle shape
  - Comparison of reaction conditions, e.g. required temperature
  - Comparison of reaction by-products
    - Moles of by-product generated per mole of reactant and product generated